

Persistent Organic Pollutants in the Dusts That Settled across Lower Manhattan after September 11, 2001

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The explosion and collapse of the World Trade Center (WTC) was a catastrophic event that produced an aerosol impacting many workers, residents, and commuters during the first few days after September 11, 2001. During the initial days that followed, 14 bulk samples of the settled dust were collected at locations surrounding the epicenter of the disaster, including one indoor location. Some samples were analyzed for many potential hazards, including inorganic and organic constituents as well as morphology. The results of the analyses for persistent organic pollutants are described herein, including polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and select organochlorine pesticides on settled dust samples. The Σ_{86} -PCBs comprising less than 0.001% by mass of the bulk in the three bulk samples analyzed indicated that PCBs were of limited significance in the total settled dust across lower Manhattan. Likewise, organochlorine pesticides, including chlordanes, hexachlorobenzene, heptachlor, 4,4'-DDE, 2,4'-DDT, 4,4'-DDT, and Mirex, were found at low concentrations in the bulk samples. Conversely, the Σ_{37} -PAHs comprised up to nearly 0.04% (<0.005–0.039%) by mass of the bulk settled dust in the six bulk samples. Further size segregation of these three initial bulk samples and seven additional samples indicates that Σ_{37} -PAHs were found in higher concentrations on relatively large particles (10–53 μm), representing up to 0.04% of the total dust mass. Significant concentrations were also found on fine particles (<2.5 μm), often accounting for ~0.005% by mass. We estimate that approximately 100–

1000 tons of Σ_{37} -PAHs were spread over a localized area immediately after the WTC disaster on September 11.

Introduction

The September 11, 2001 (9/11) attack on the World Trade Center (WTC) resulted in an intense fire and the subsequent complete collapse of both structures and damage to adjacent buildings. A consequence of the burning and pulverization of buildings was the development of a large plume of dust and smoke that released both particles and gases into the atmosphere. The initial plume was initially dispersed in all directions from ground zero and later to many outdoor and indoor locations downwind. For the first 12–18 h after the collapse, the winds transported the plume to the east and then to the southeast toward Brooklyn (1).

To begin the process of assessing the possible impacts of the dust and smoke in Lower Manhattan during the first few days after the disaster, samples of particles that initially settled in downtown NYC were taken from 13 locations around the WTC site. Four samples were collected on September 12, and six samples were taken on September 13. Further, two samples were taken on September 16, and one additional sample was taken on September 17. The purpose for collecting the samples was to determine the chemical and physical characteristics of the material that were present in the initial plume and to determine the absence or presence of contaminants that could affect acute or long-term human and ecosystem health. The compounds and materials present in the plume were expected to be similar to those found in building fires or collapsed buildings. The primary differences are the intensity of the fire (as compared with normal building fires), the occurrence of a building collapse in conjunction with these fires, and the extremely large mass of material (~1 $\times 10^6$ ton) reduced to dust and smoke (2, 1). A summary of the potential hazards (3) as well as a list of initial steps taken to assess human health exposure during and after the disaster are outlined elsewhere (4, 1).

Initial measurements focused on the general composition of the dust and smoke, with a primary concern being asbestos (3). The approach employed for initial characterizations (Phase I of the work described here) focused upon analyzing three dust samples, utilizing a wide battery of tests and methodologies. The organic analyses described herein accompany the battery of additional Phase I measurements of the soluble ions, trace metals, and organic components of the mass as well as a general and morphological characterization of the percent distribution of various materials present in each sample. Results of the Phase I morphological, organic, and inorganic analyses are reported elsewhere (1) but will be briefly summarized below. Subsequent, chemical analysis focused upon the compounds of greatest concern for the second phase of analysis of samples. A majority of the samples analyzed in the second phase were sieved, resuspended in air, and size segregated according to aerodynamic equivalent diameter (aed). The concentrations of organic compounds found in both Phase I and Phase II analyses are discussed and placed into context of relevant ambient measurements.

Methods

Sample Collection. Four bulk settled dust/aerosol samples were collected on September 12, by NYU (Park Row at Spruce Street; Church Street at Vesey Street; Hilton Hotel on Church Street; and Church Street at Maiden Lane). The following

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TABLE 1. List of Samples by Date Collected

date collected	label	sample location	size fraction used in chemical analysis	analysis performed as part of this work ^b
Sept 12, 2001	A	Park Row and Spruce Street	<2.5, 10–53, and >53 μm	PAH
Sept 12, 2001	B	Church Street and Vesey Street	bulk	PAH
Sept 12, 2001	C	55 Church Street	bulk	PAH
Sept 12, 2001	D	Church St. and Maiden Lane	bulk	PAH
Sept 13, 2001	E	Cortland Station at Church Street	<2.5 and 10–53 μm	PAH
Sept 13, 2001	F	Rector and Trinity	<2.5 and 10–53 μm	PAH
Sept 13, 2001	G	North Cove – Winter Garden Park	<2.5 and 10–53 μm	PAH
Sept 13, 2001	H	North End Avenue between Murray and Warren	<2.5 and 10–53 μm	PAH
Sept 13, 2001	I	Murray and Greenwich	<2.5 and 10–53 μm	PAH
Sept 13, 2001	J	120 Broadway ^a	<2.5 and 10–53 μm	PAH
Sept 16, 2001	K	Cherry Street and Market Street	bulk	PAH, PCB, OC pesticides ^b
			<2.5 and 10–53 μm	PAH
Sept 16, 2001	L	Market Street and Water Street	bulk	PAH, PCB, OC pesticides ^b
			<2.5 and 10–53 μm	PAH
Sept 17, 2001	M	Cortland Street	bulk	PAH, PCB, OC pesticides ^b
			<2.5 and 10–53 μm	PAH

^a Indicates sample collected at an indoor location. ^b See ref 1 for further analyses, including quantification of inorganics, volatile organics, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and morphological character of bulk samples collected on September 16 and 17.

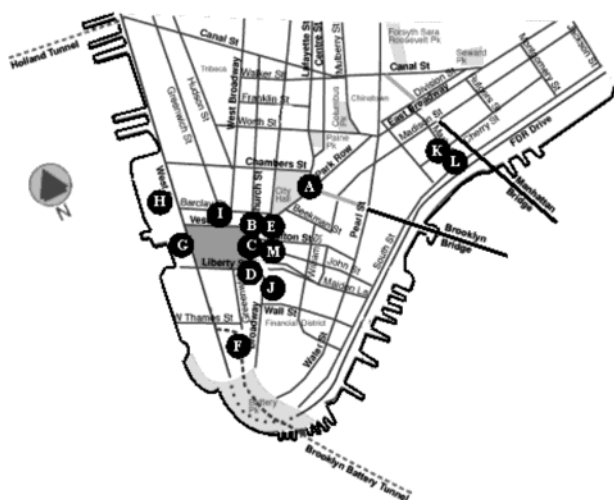


FIGURE 1. Map of detailing locations around lower Manhattan at which dust samples were collected. Letters indicate samples collected on September 12, 13, 16, and 17, 2001.

day, on September 13, 2001, five outdoor and one indoor bulk settled dust/aerosol samples were collected at Cortland Station at Church Street; Rector and Trinity; Winter Garden Park in North Cove; North End Avenue between Murray and Warren; and Murray and Greenwich; and one sample was collected from the interior of 120 Broadway (see Figure 1 and Table 1). Three days later on September 16, two additional bulk samples were collected from 10 to 15 cm thick deposits that were on the top of two cars, located one and two city blocks west of the East River between the Manhattan and Brooklyn Bridges, on Cherry Street and Market Street, respectively. On the 17th of September, one additional sample was collected first from external ledges around the entrance of a building on Cortland Street one block east of the WTC building complex. In all cases, samples were collected using the protocols established for surface soil collection in studies of the dispersal of Cr laden hazardous waste in Jersey City, NJ (5), and the National Human Exposure Assessment Survey (6). After collection, all samples were stored at 4 °C prior to delivery of subfractions to collaborators' laboratories for analysis.

Sample Preparation. The analyses conducted on each settled dust sample as part of Phase I were based upon the nature of the sources of the particles that were aerosolized on 9/11. The analytical procedures utilized included qualita-

tive and quantitative analyses to detect construction and furnishing debris as well as combustible materials and products of incomplete combustion. Phase I analyses were designed to provide a general, broad characterization of the content of the samples using a combination techniques. This work provided an opportunity to classify the general morphology and focus the chemical analyses subsequently performed on each sample. The inorganic analyses included trace and toxic elements, ionic species, and functional groups. The organic chemical analyses included polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), select organochlorine pesticides, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, phthalates, and hydrocarbons. Only the findings from the PAH, PCB, and pesticide analyses are presented in detail here. A summary of these results in relation to the inorganic analyses and additional organic analyses as well as asbestos, alpha and Beta radio-nuclide activity, and morphology are presented elsewhere (1). The limited quantity of each sample required that the compositional analyses of these samples focus on only those species that had the potential for the greatest human exposure and health concern, as indicated by the initial analyses. Upon completion of Phase I analyses, classification and determination decisions were made, resulting in Phase II organic chemical analyses focusing on PAH concentrations in 10 size segregated, resuspended dust samples and three additional bulk settled dust samples.

Size Fractionation. Seven of the above bulk samples were size fractionated by sieving for particles greater than 53 μm in diameter followed by resuspension in air and subsequent size classification based upon aerodynamic equivalent diameters (aed) in a cyclone. The WTC dusts were first mechanically separated using a sieve with a mesh size of 53 μm . The fraction of particles that were smaller than 53 μm were further separated, aerodynamically, into three size fractions (53–10 μm aed, 10–2.5 μm aed, and <2.5 μm aed). Particles were resuspended by a jet of clean, filtered air, passing through an inlet (Wedding Inlet, 10 μm cut size, Anderson Instrument) before entering a cyclone with an aerodynamic cut size of 2.5 μm (BGI, Inc). Particles between 2.5 and 10 μm aed were collected by the cyclone, while particles smaller than 2.5 μm aed, which penetrated through the cyclone, were collected on downstream Teflon filters.

For the outdoor samples, more than 98 wt % of the dusts were larger than 10 μm aed, with more than 57% greater than 53 μm diameter. For the single indoor sample (site J; inside 120 Broadway) more than 96 wt % of the bulk dusts was larger than 10 μm aed, and only 18% was greater than

53 μm diameter. In all outdoor and the single indoor, size segregated samples, the mass of material collected in the 2.5–10 μm aed, size fraction (<0.3 wt % in every sample) was not sufficient to adequately perform organic chemical analyses.

Quantitative Chemical Analysis. (a) *Polychlorinated Biphenyl and OC Pesticides.* Triplicate aliquots of ~ 0.7 g of each of the three settled dust samples (samples K, L, and M) were also ultrasonically extracted in 30 mL of dichloromethane, reduced in volume, and fractionated on a column of 3% water deactivated alumina and reduced in volume. Samples were injected with a solution containing 50 ng of PCB congeners 30 and 204 (2,4,6-trichlorobiphenyl and 2,2',3,4,4',5,6,6'-octachlorobiphenyl, respectively), as internal standards prior to analysis by gas chromatography/electron capture detection on a Hewlett-Packard 6890 equipped with a ^{63}Ni electron capture detector for quantification of 68 polychlorinated biphenyl congeners, hexachlorobenzene, DDTs (4,4'-DDE, 2,4'-DDT, and 4,4'-DDT), and Mirex according to the procedures of Brunciak et al. (7). All compounds were identified and quantified against known concentrations of authentic standards as described by Mullins (8). Like the PAH analysis, NIST Standard Reference Material 1649a – Urban Dust, Organics (9) was processed in parallel with each sample for comparison and verification of results. Procedural blank samples (i.e. 0 g of dust) were also processed in parallel with samples in order to quantify the overall operational limits of detection for the procedures. This PCB/OC pesticide analysis was performed as a portion of the Phase I analyses described above but were not included in Phase II characterizations.

(b) *Polycyclic Aromatic Hydrocarbons and Chlordanes.* Additional triplicate aliquots of ~ 0.7 g of each settled dust sample were weighed, ultrasonically extracted in 30 mL of dichloromethane, reduced in volume under a gentle stream of clean, dry nitrogen, and injected with a solution containing 100 ng each of four perdeuterated internal standards. These samples were analyzed by gas chromatography/mass selective detection on a Hewlett-Packard 6890/5973 for 37 individual PAHs and six chlordane species utilizing well-established methods (10, 11). The mass selective detector was operated in selective ion monitoring mode with an electron impact ionization energy of 70 eV. The 37 PAHs reported herein are as follows: naphthalene, acenaphthylene, acenaphthene, fluorene, 1-methylfluorene, dibenzothiophene, phenanthrene, anthracene, methylphenanthrenes + methylanthracenes (the sum of 1-methylphenanthrene, 2-methylphenanthrene, 1-methylanthracene, 2-methylanthracene, and 9-methylanthracene), 4,5-methylenepheneanthrene, 3,6-dimethylphenanthrene, 9,10-dimethylanthracene, fluoranthene, pyrene, benzo[a]fluorene, retene, benzo[b]fluorene, cyclopenta[cd]pyrene, benz[a]anthracene, chrysene + triphenylene, naphthacene, benzo[b]naphtho[2,1-d]thiophene, benzo[b]fluoranthene + benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene + dibenz[ac]anthracene, benzo[g,h,i]perylene, and coronene. The chlordane species reported herein as the sum of chlordanes (Σ -chlordanes) include the following: oxy-chlordane, trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor, and MC5. All compounds were identified and quantified against standard solutions containing known concentrations of authentic compounds and where possible compared to NIST Standard Reference Material 1649a, Urban Dust, Organics (9), which was processed in parallel with each sample for comparison and verification of results. Procedural blank samples (i.e. 0 g of dust) were also processed in parallel with samples in order to quantify the overall operational limits of detection for the procedures. This GC/MS procedure for quantifying PAHs was utilized in the analysis of both Phase I (bulk) and Phase

II (size segregated) samples, with the single exception that the entire mass in each size segregated sample was utilized in a single analysis regardless of whether it amounted to 0.7 g.

Quality Assurance. Surrogates. Average percent recoveries of 50 ng of four PCB congeners added to each of the three samples analyzed in triplicate as part of Phase I measurements were $79 \pm 4\%$, $83 \pm 5\%$, $84 \pm 5\%$, and $89 \pm 5\%$ for nonindustrially produced, IUPAC congener numbers 14, 23, 65, and 166, representing 3,5-dichlorobiphenyl, 2,3,5-trichlorobiphenyl, 2,3,5,6-tetrachlorobiphenyl, and 2,3,4,4',5,6-hexachlorobiphenyl, respectively. Similarly, average percent recoveries of perdeuterated PAHs utilized as surrogate standards (± 1 standard deviation) added to each sample were as follows: $63 \pm 6\%$, $82 \pm 8\%$, $89 \pm 5\%$, and $80 \pm 8\%$ for acenaphthene- d_{10} , anthracene- d_{10} , fluorene- d_{10} , and pyrene- d_{12} . Similarly, average percent recoveries (± 1 standard deviation) of surrogate standards were as follows: $76 \pm 18\%$, $80 \pm 11\%$, $92 \pm 20\%$, and $98 \pm 19\%$ for acenaphthene- d_{10} , anthracene- d_{10} , fluorene- d_{10} , and pyrene- d_{12} , respectively, in Phase II measurements. These surrogate recoveries indicate that there were limited sample losses during processing and handling. The concentrations reported herein have not been corrected to account for the minimal losses indicated by the surrogate recoveries.

Blanks. Chemical analysis of procedural and laboratory blanks indicated that background levels of Σ_{68} -PCBs were 1.1 ± 0.3 ng and Σ_{37} -PAHs were 2.9 ± 0.5 ng in Phase I measurements. Masses of Σ_{37} -PAHs were 3 ± 0.5 ng in Phase II measurements. For Phase I measurements, this translates into limits of detection (as the average plus three standard deviations) for analysis of 1 g of dust equal to 2.0 ng/g for Σ_{68} -PCBs and 4.4 ng/g for Σ_{37} -PAHs. Likewise, operational limits of detection for Σ_{37} -PAHs equal 4.5 ng/g for a 1 g sample of dust in Phase II analyses.

Comparisons to SRMs. Chemical analyses of standard reference materials in parallel with samples allows for direct assessment of extraction, handling, and quantitative methods utilized in this work. Of the 37 compounds measured here, there are 16 for which certified concentrations have been determined (9). A linear correlation of the average concentrations measured via the methods described above ($n = 3$) vs the certified values results in a significant correlation ($p < 0.001$; $R^2 = 0.979$). The resulting slope of this correlation (with both expressed as ng/g) was equal to 1.00 ± 0.04 ($p < 0.001$), and the intercept was not different than zero (168 ± 172 ; $p = 0.32$). The concentrations measured in SRM 1649a generally fall within the reported uncertainties for the certified concentrations (9). Thus, based upon these analyses of SRM 1649a, we conclude that the sample handling and analysis techniques used here represent accurate measurements of the true concentrations in the dusts and furthermore do not introduce significant biases into the results reported here.

Results and Discussion

Phase I Analysis of Bulk Dust Samples. The three bulk samples (Market Street, Cherry Street, and Cortland Street) that were analyzed in triplicate by both GC/MS and GC/ECD resulted in concentrations for PCBs, PAHs, organochlorine pesticides, and chlordanes (Table 2). Additional analyses, including asbestos, other organic species, water soluble ions, toxic metals, and morphological character, are available for these three samples elsewhere (1). Concentrations of the sum of 68 polychlorinated biphenyl congeners (Σ_{68} -PCBs) in the three bulk samples collected September 16 and 17, 2001, average 667 ± 113 ng/g and range from 562 ± 63 (site K; Cherry St. and Market St.) to 723 ± 77 ng/g (site L; Market St. and Water St.). These concentrations are not different from the measured concentrations of PCBs on aerosols in Jersey City, NJ, which average 890 ± 760 ng/g of aerosol (n

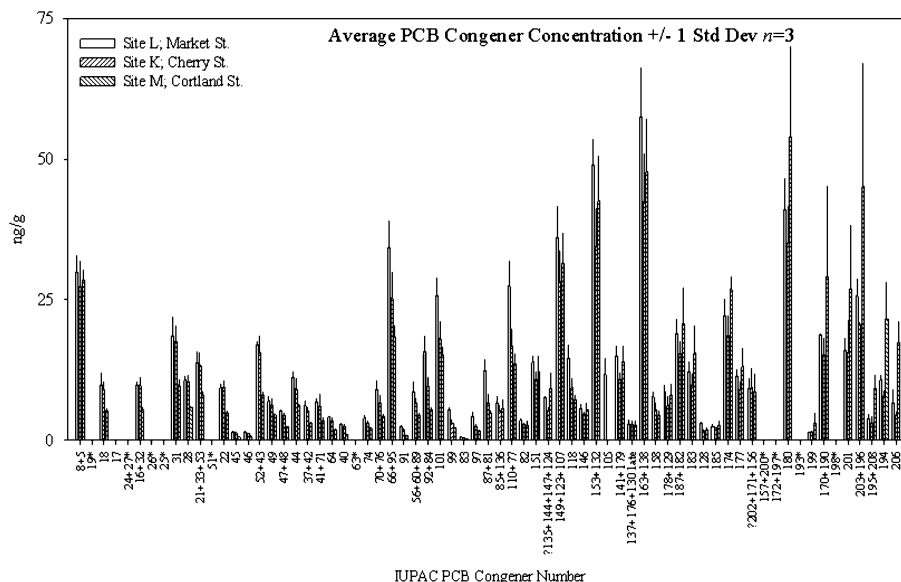


FIGURE 2. PCB fingerprints of three bulk settled dust samples collected in lower Manhattan on September 16 and 17, 2001.

TABLE 2. Measured Concentrations (ng/g) of Select Semivolatile Organic Compounds in Phase I Bulk Samples Collected on September 16 and 17, 2001, around Lower Manhattan

	K Cherry St. and Market St. Sept 16, 2001 [ng/g]	L Market St. and Water St. Sept 16, 2001 [ng/g]	M Cortland St. Sept 17, 2001 [ng/g]
Σ_{89} -PCB (w/o 8+5)	562	723	631
Σ_{88} -PCB (w/ 8+5)	589	753	659
Σ_{37} -PAH	218 000	376 000	383 000
Selected PAHs			
fluorene	2620	32 200	6800
phenanthrene	22 300	32 100	44 100
fluoranthene	13 700	32 600	40 300
benzo(a)pyrene	12 100	19 300	23 000
benzo(b+k)- fluoranthene	15 600	29 500	36 600
Pesticides			
heptachlor	nd	nd	nd
4,4-DDE	2.1	3.0	1.3
2,4-DDT	nd	nd	nd
4,4-DDT	nd	nd	nd
Mirex	0.8	nd	nd
Σ -chlordanes	5.6	3.7	3.1

= 78) over the period 7/5/98–1/19/01. These measurements were made as part of the New Jersey Atmospheric Deposition Network (NJADN) and are summarized elsewhere (7). PCB congener patterns in these three bulk dust samples were dominated by congeners 180, 163+138, 153+132, and 149+123+107 (Figure 2). This congener pattern is in contrast to that found on ambient aerosols in Jersey City, NJ (7), which was dominated by congeners 163+138, 66+95, 52+43, and 180, generally representing a lighter mixture of PCB congeners than that which was seen in the three dust samples presented here.

Concentrations of hexachlorobenzene in the three bulk samples collected on September 16, 2001, average 1.3 ± 0.4 ng/g and range from 0.9 ± 0.2 (site K; Cherry St. and Market St.) to 1.8 ± 0.1 ng/g (site M; Cortland St.). These concentrations are lower than those on ambient aerosols in Jersey City NJ, which average 8.1 ± 10.0 ng/g ($n = 74$ over the period of 7/5/98 through 1/19/01). Concentrations of 4,4'-DDT and 2,4'-DDT in these three bulk samples collected September

16 and 17, 2001, are below the levels measured in laboratory blanks processed in parallel with these samples. Only 4,4'-DDE was found at concentrations above limits of detection in all analyses, averaging 2.2 ± 0.9 ng/g and ranging from 1.3 ng/g ± 0.8 (site M; Cortland St.) to 3.0 ± 0.5 ng/g (site L; Market St. and Water St.). Similar to DDT, heptachlor was below limits of detection in these samples from sites K, L, and M. Concentrations of the sum of five chlordane species (Σ -chlordanes) in the three dust samples collected on September 16, 2001, average 3.6 ± 0.4 ng/g and range from 3.3 ± 0.1 ng/g (site M; Cortland St.) to 3.7 ± 0.5 ng/g (site K; Cherry St. and Market St.). These concentrations are much lower than those measured in Jersey City, NJ through the NJADN program (159 ± 111 ng/g, $n = 30$ over the period 7/5/98–3/30/99 (12)).

Concentrations of the sum of 37 individual polycyclic aromatic hydrocarbons (Σ_{37} -PAHs) average $326\,000 \pm 107\,000$ ng/g (0.033 ± 0.011 wt %) and range from $218\,000 \pm 56\,000$ ng/g (site K; Cherry St. and Market St.) to $383\,000 \pm 97\,000$ ng/g (site M; Cortland St.) in the three bulk dust samples (sites K, L, and M). Measured concentrations of PAHs in these three bulk dust samples are high, especially in light of the extremely large masses of dust generated in this disaster. Concentrations of these same PAH species at a long-term monitoring site in Jersey City, NJ average $107\,000 \pm 13$ ng/g of total suspended particulate matter (TSP) over the period spanning from 7/5/98 to 1/19/01 (13). Bulk dust associated PAHs were dominated by phenanthrene, fluoranthene, pyrene, and benzo[b+k]fluoranthene (see Figure 3). In contrast, PAH fingerprints in ambient air over Jersey City, NJ were dominated by benzo[b+k]fluoranthene, methylphenanthrenes, indeno[123,cd]pyrene, chrysene+triphenylene, benzo[ghi]perylene, and coronene.

The total concentrations of 37 individual PAHs represented up to nearly 0.04% by mass of the bulk settled dusts measured as part of Phase I (samples K, L, and M). The levels of individual PAH ranged from hundreds of pg/g to >40 μ g/g. Of the three initial bulk samples analyzed as part of Phase I, the highest concentrations of the 37 individual PAHs were found in the Cortland Street sample and the sites closest to the fires after the collapse. The large variety of fires associated with the disaster would be expected to have burned at differing temperatures, thus leading to a range of unburned and partially burned hydrocarbons derived from the diverse mix of plastics, metals, woods, and other synthetic products in the collapsed buildings. In light of the extreme quantity

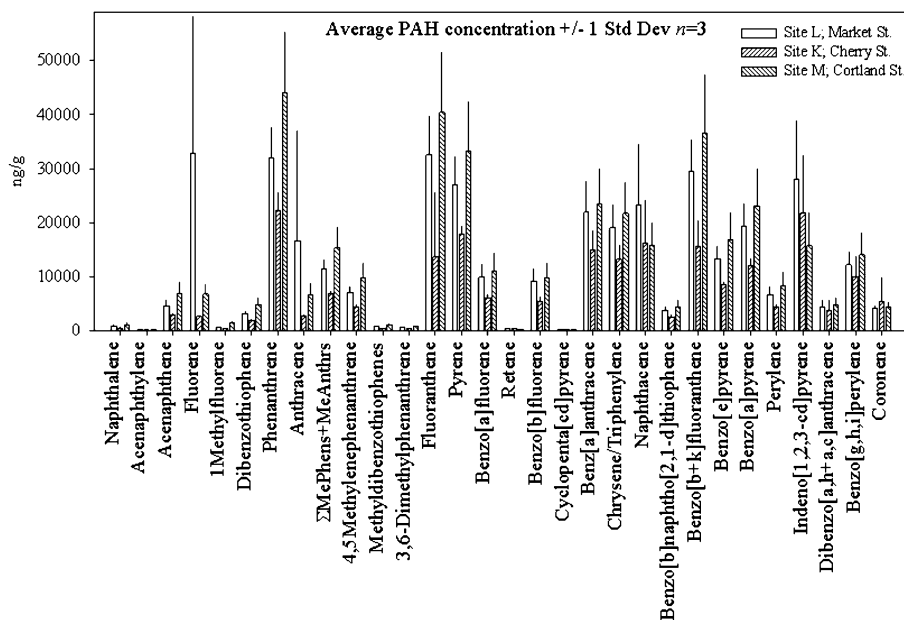


FIGURE 3. PAH fingerprints of three bulk settled dust samples collected in lower Manhattan on September 16 and 17, 2001.

of dust created in the disaster coupled with the high concentrations of PAHs, subsequent analysis of dust samples for organic contaminants focused entirely upon PAHs.

Phase I: Results for Other Compounds. Concentrations of various other compounds and elements were determined for these three bulk samples (sites K, L, and M), including pH, mass size distributions, asbestos content, toxic and trace metals, polychlorinated dibenzodioxins, and dibenzofurans as well as a suite of semivolatile hydrocarbons. Briefly, concentrations of asbestos were between 0.8 and 3.0%, while concentrations of individual metals ranged from less than 1500 ng/g (Bi) to 4000–8000 ng/g (U, Cd,) to nearly 3 000 000 ng/g (Zn). Additional organic analysis results found PCDD and PCDF 2,3,7,8-dioxin total equivalents (TeQs) were in the range of 96–104 ng/kg as well as notable concentrations of phthalates and unburned hydrocarbon residuals. More than the 37 individual PAHs reported here were detected in Phase I analyses. For a complete discussion of all methods and results pertaining to these three initial bulk samples, we refer the reader to ref 1.

Phase II: Analysis of Size-Fractionated Samples. Due to the high concentrations of PAHs, subsequent analysis of resuspended size segregated dust samples for organic contaminants focused upon the 37 PAHs listed above. For the outdoor samples, more than 98 wt % of the dusts were larger than 10 μm aed, with more than 57% greater than 53 μm diameter (Figure 4). For the single indoor sample (site J; 120 Broadway) more than 96 wt % of the bulk dusts was larger than 10 μm aed, with only 8% greater than 53 μm diameter.

Concentrations of Σ_{37} -PAHs on various size fractions collected at sites in all four cardinal directions from the epicenter of the disaster range from 19 000 to 367 000 ng/g (Figures 5 and 6). In general, the 10–53 μm size fraction contained higher concentrations than the corresponding fine particle fractions, with the exception of the samples collected at site I (Murray St. and Greenwich St.), which exhibited higher concentrations of Σ_{37} -PAHs in the fine fraction (Table 3). Due to the limited quantity of sample available and the very low mass concentrations of particles in the 2.5–10 μm aed size range, no attempt was made to quantify the concentrations of these Σ_{37} -PAHs in this size range.

Σ_{37} -PAH concentrations represent up to 0.04% of specific particle size fractions of the mass of the settled dust in Lower Manhattan. Though concentrations of individual PAHs vary

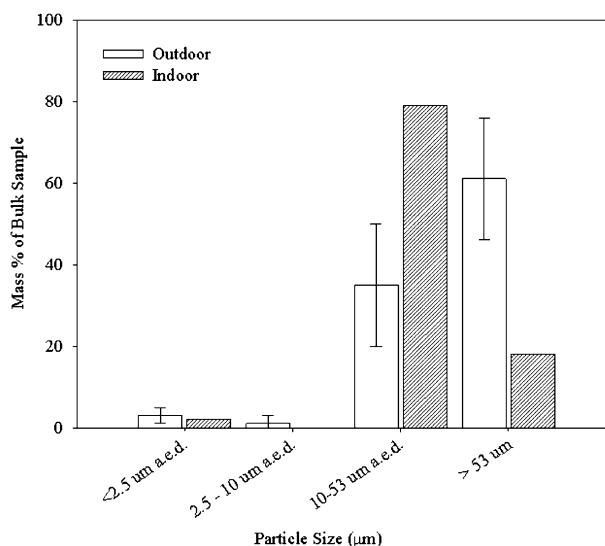


FIGURE 4. Mass size distribution of resuspended settled dusts collected on September 12 and 13, 2001, around lower Manhattan.

greatly throughout the size-segregated samples, the relative pattern varies little, indicating that the settled dusts, which spread over lower Manhattan, were relatively homogeneous, with variations in concentration but not in “source”. Thus the emitted PAHs were sorbed onto particles of varying sizes and spread throughout lower Manhattan and beyond.

Three additional bulk samples analyzed as part of Phase II (sites B, C, and D) represent a north to south transect down Church St., along the east side of the epicenter of the disaster. The concentrations of Σ_{37} -PAHs increase from north to south along Church Street, which can be understood by recalling the wind direction immediately after the disaster. The wind blew to the east/northeast during the first 12–18 h after the disaster, carrying debris, dust, and smoke to the East River and beyond. Thereafter, the winds shifted and blew from the north to the south, carrying the dusts over Battery Park and south over New Jersey (1). Thus, we see an increase in the concentrations of PAHs from north to south, as the settled dusts may represent more combustion byproducts from the numerous fires that burned continuously following the initial explosions and building collapses.

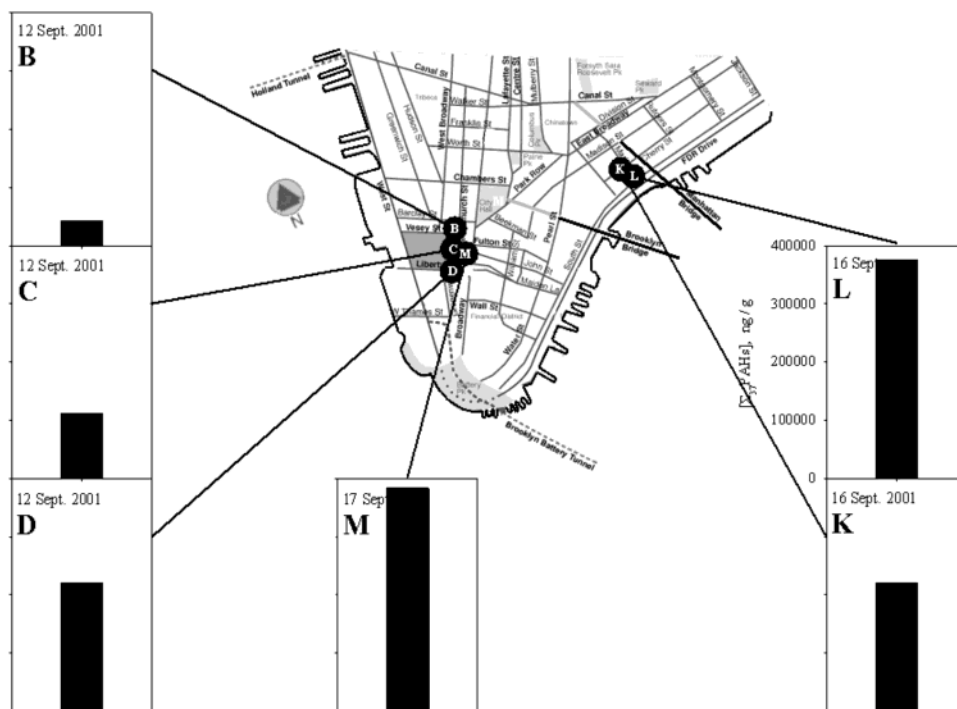


FIGURE 5. Concentrations of Σ_{37} -PAHs on bulk settled dust samples collected around lower Manhattan on September 12, 16, and 17, 2001.

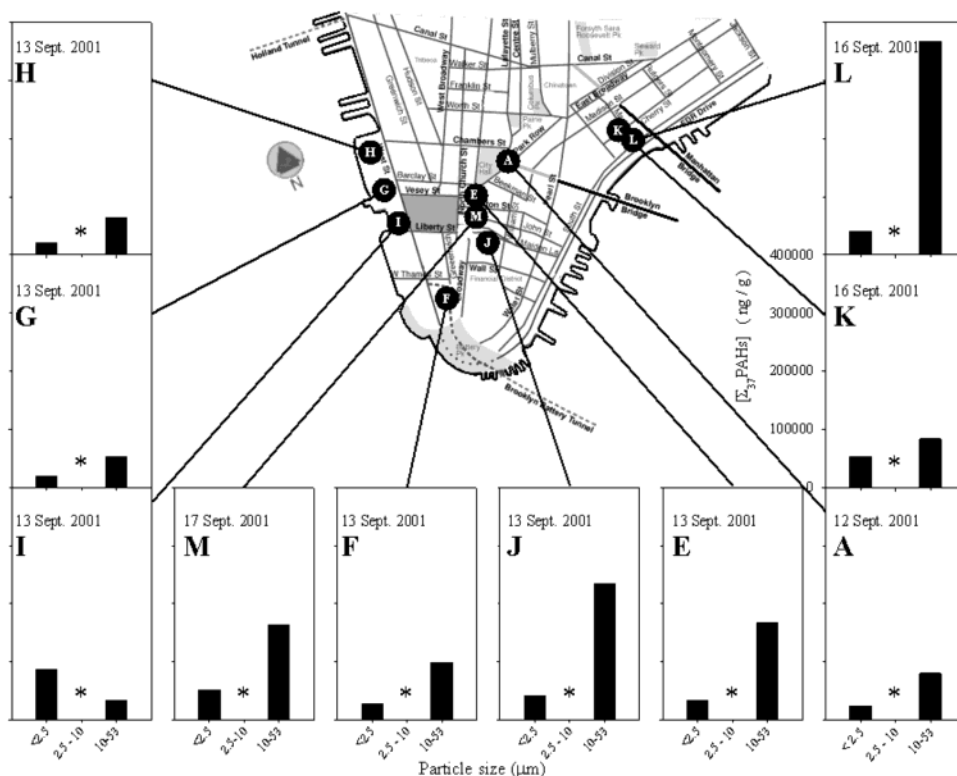


FIGURE 6. Concentrations of Σ_{37} -PAHs on size fractionated, resuspended settled dust samples collected around lower Manhattan on September 12, 13, 16, and 17, 2001. Note: * indicates that insufficient mass was collected to successfully analyze the 2.5–10 μm size fraction.

These measurements of the concentrations of PAHs on settled dusts, in conjunction with initial calculations of the mass of debris involved in the disaster, can be used to estimate the total burden of Σ_{37} -PAHs spread over a currently undefined area encompassing lower Manhattan. Using an estimate of total PAH concentration of 0.01–0.1% by mass and an estimate of 1×10^6 tons of material, we can estimate that approximately 100–1000 tons of Σ_{37} -PAHs were spread

over an unknown area immediately after the WTC disaster on September 11, 2001. This estimate is based upon the bulk concentrations in settled dusts analyzed in Phases I and II of this work. However, the estimate of the total dust emitted, and the fraction that settled (and where), may represent greater uncertainties surrounding this initial estimate of total ecosystem loadings and the resulting ecosystem impacts.

TABLE 3. Concentrations of Σ_{37} -PAHs in Samples

date collected	label	sample location	size fraction analyzed	$[\Sigma_{37}\text{-PAHs}]$ ng/g
Sept 12, 2001	A	Park Row and Spruce St	<2.5 μm 10–53 μm >53 μm	24 500 79 900 346 200
Sept 12, 2001	B	Church St. and Vesey St.	bulk	42 000
Sept 12, 2001	C	55 Church Street	bulk	112 000
Sept 12, 2001	D	Church St. and Maiden Lane	bulk	221 000
Sept 13, 2001	E	Cortland Station at Church Street	<2.5 μm 10–53 μm	34 100 167 000
Sept 13, 2001	F	Rector and Trinity	<2.5 μm 10–53 μm	28 100 98 500
Sept 13, 2001	G	North Cove – Winter Garden Park	<2.5 μm 10–53 μm	19 000 52 900
Sept 13, 2001	H	North End Avenue between Murray and Warren	<2.5 μm 10–53 μm	20 800 64 000
Sept 13, 2001	I	Murray and Greenwich	<2.5 μm 10–53 μm	86 200 33 400
Sept 13, 2001	J	120 Broadway ^a	<2.5 μm 10–53 μm	40 700 233 000
Sept 16, 2001	K	Cherry St. and Market St.	bulk ^b <2.5 μm 10–53 μm	218 000 61 300 83 500
Sept 16, 2001	L	Market St. and Water St.	bulk ^b <2.5 μm 10–53 μm	376 000 40 800 367 000
Sept 17, 2001	M	Cortland Street	bulk ^b <2.5 μm 10–53 μm	383 000 51 600 164 100

^a Indicates sample collected at an indoor location. ^b See ref 1 for further analyses, including quantification of inorganic metals and ions, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and morphological character of bulk samples collected on September 16 and 17.

The sets of settled dust/smoke samples collected around lower Manhattan provide valuable information on the initial composition and the immediate human and ecosystem health concerns arising from the WTC disaster. The vast majority of the bulk mass was pulverized building and construction materials including cement, cellulose, and glass fibers (1). However, the fires after the explosion and collapse produced aerosol particles from pulverized building debris and contents of various products of incomplete combustion. This is not unexpected because of the wide variety of plastics, woods, furnishings, and business machines, and computers. Semivolatile organic contaminants with significant concentrations or surface loadings included polycyclic aromatic hydrocarbons. The identification of the major components is important for assessing acute inhalation of resuspendable dust and direct inhalation during the first days after the attack. The PAH levels detected in these samples indicate the need for better characterization of longer term consequences of outdoor and indoor human exposure and ecosystem exposure to byproducts of incomplete combustion associated with the collapse and fires at the WTC. The levels of PCBs are similar to those found in the general environment, while select organochlorine pesticide concentrations were found to be well below average ambient concentrations.

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our sympathy and continuing concern for the survivors and for the families of the victims of September 11, 2001.

Supporting Information Available

Concentrations of individual PAHs measured in settled dust samples from across lower Manhattan. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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